Reaction and Transport in Gas Diffusion Electrodes of Li-O_2 batteries: Experiments and Modeling

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II. Continuum model of an aqueous Li-O_2 system

III. Model parameterization

IV. Model validation

V. Electrode and cell design

VI. Summary

I. Motivation and background

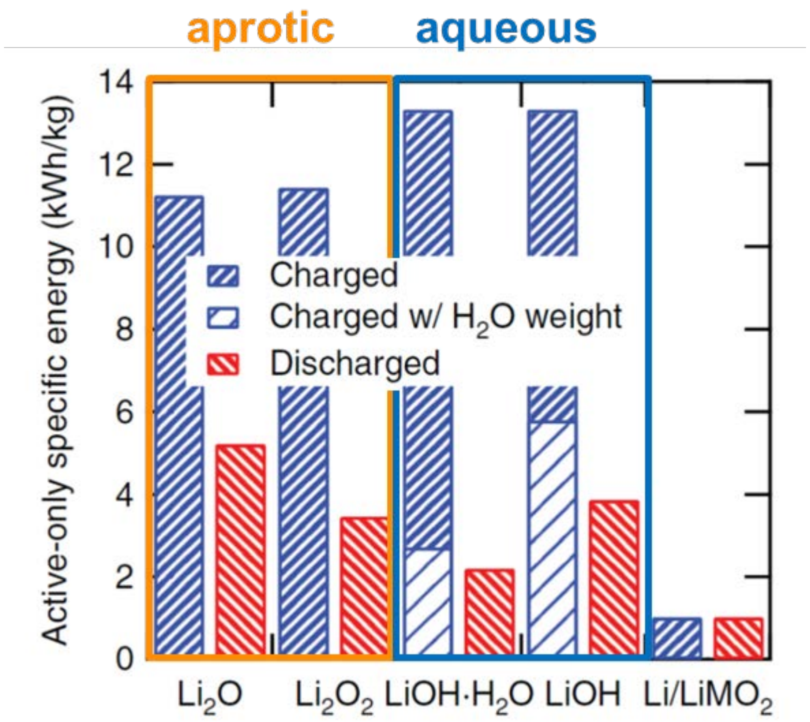
- Proposed designs
  - **Aprotic** Li-O_2 batteries $(U = 3\ \mathrm{V})$

    $$O_2 + 2\,Li^+ + 4\,e^- \rightleftarrows Li_2O_2^{(s)}$$

    - **Stable electrolyte?**
    - Solubility and diffusivity of O_2?
    - Insulating discharge products
  - **Aqueous** Li-O_2 batteries $(U = 3.45\ \mathrm{V})$

    $$O_2 + 2\,H_2O + 4\,e^- \rightleftarrows 4\,OH^-$$

    - **Stable anode protection?**
    - Precipitation of $LiOH \cdot H_2O$
    - Advantage: GDEs
  - …



Christensen, J. *et al*. *J. Electroch. Soc.* **159**, R1 (2012).

➔ **Very high theoretical energy densities**

I. Motivation and background

- Porous <u>G</u>as <u>D</u>iffusion <u>E</u>lectrode

  $$\mathbf{O_2 + 2\,H_2O + 4\,e^- \rightleftarrows 4\,OH^-}$$

  - High surface area
  - Fast transport of O_2
  - ➔High current densities

- Lithium metal anode

  $$\mathbf{Li \rightleftarrows Li^+ + e^-}$$

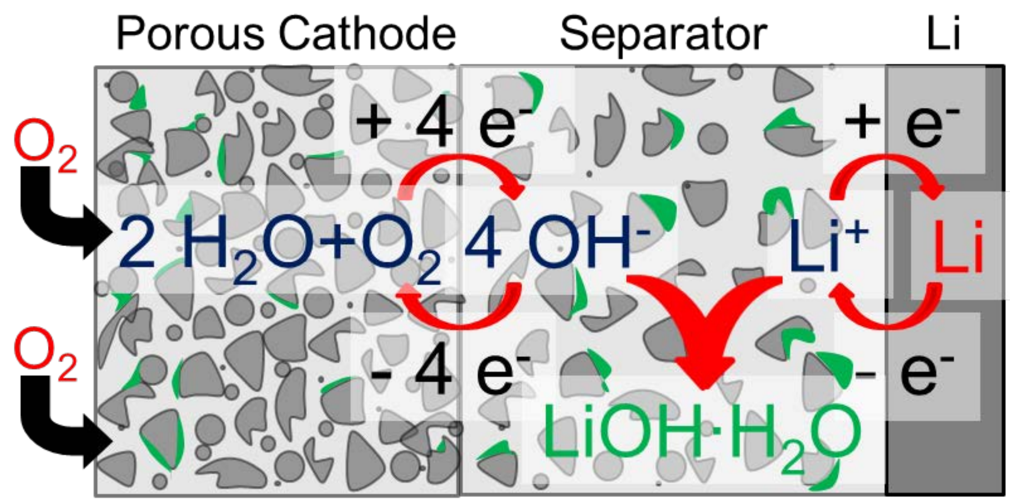
  - Stable anode protection

- Separator
  - Precipitation of $LiOH \cdot H_2O$ ($c_s = 5.3\,\frac{\mathrm{mol}}{\mathrm{l}}$)

  $$\mathbf{Li^+ + OH^- + H_2O \rightleftarrows LiOH \cdot H_2O^{(s)}}$$

  - Clogging of transport pathways

Design of **aqueous** Li-O_2 batteries



II. Continuum modeling

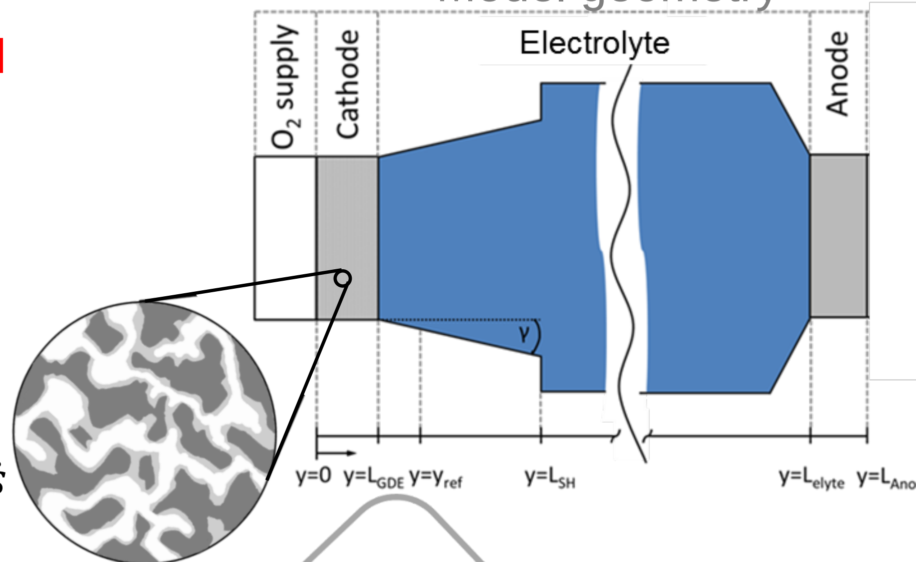
- 1D spatially resolved **continuum model**
- Transport in liquid electrolyte
  - **Concentrated solution theory**
  - Electro-neutrality condition
  - **Darcy flow** $\vec{v} = -B/\mu \cdot \mathrm{grad}\, p_{\mathrm{liq}}$

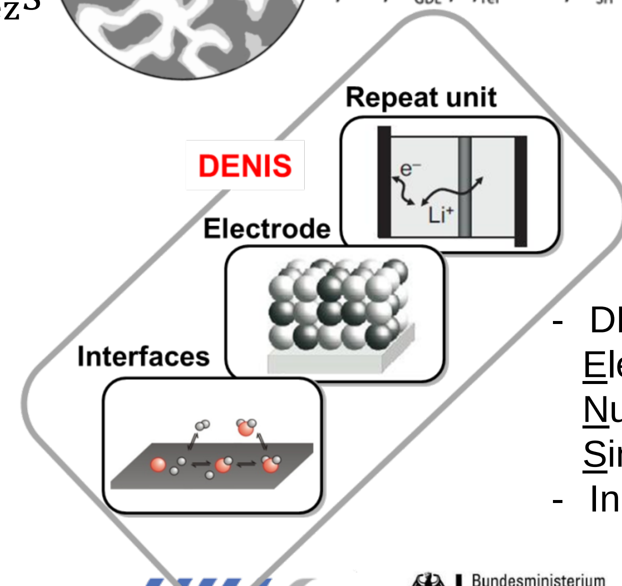
$$\frac{\partial(\epsilon_{\mathrm{liquid}} c)}{\partial t} = -\mathrm{div}(\vec{v}\epsilon_{\mathrm{liq}} c) - \mathrm{div}\vec{j} + A_{\mathrm{spez}}\dot{s}$$

- **Global kinetics** (Butler-Volmer type)
  - ➔ ORR/OER
- **Single set of parameters**
  - ➔ Literature or own experiments

➔ Simulation software **DENIS**

Model geometry





- DENIS: Detailed Electrochemistry and Numerical Impedance Simulation
- In-house software

Horstmann, B. *et al. Energy Environ. Sci.* **6**, 1299–1314 (2013).
Neidhardt, J. P. *et al. J. Electrochem. Soc.* **159**, A1528 (2012).
Bessler, W. G. *et al. Electrochim. Acta* **53**, 1782–1800 (2007).

II. Continuum modeling - Transport in porous media

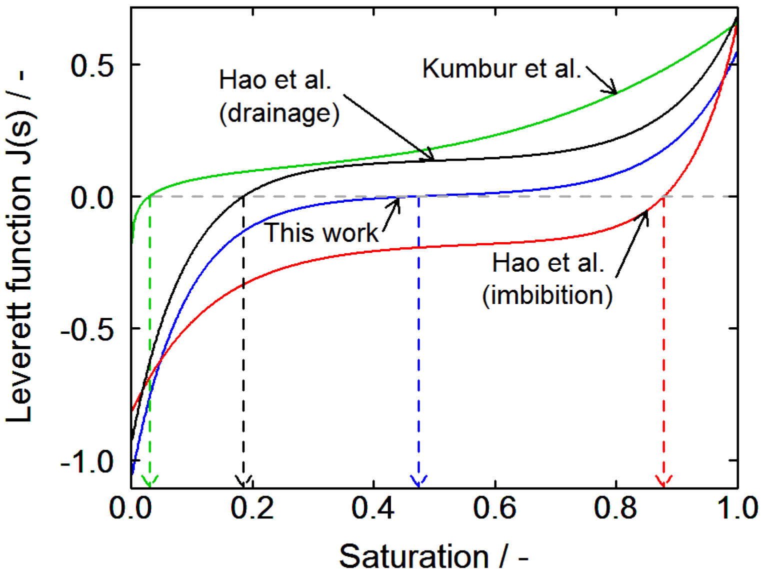
- Effective transport properties
  - Bruggeman equation:

$$D_j^{eff} = D_j^0 \cdot \varepsilon_{\mathrm{liq}}^{\beta} = D_j^0 \cdot (\varepsilon^0 s)^{\beta}$$

- Capillary pressure in porous electrodes

$$p_c = p_{\mathrm{gas}} - p_{\mathrm{liq}} = -\sigma_t \sqrt{\varepsilon^0/_k}\ J(s)$$

  - Constant Total Volume $\sum_k \varepsilon_k(p_k) = 1$
  - **Liquid equation of state:** $\sum_s \frac{\partial V_{\mathrm{liquid}}}{\partial N_s} c_s = 1$
  - Gas equation of state: $p_{\mathrm{gas}} V_{\mathrm{gas}} = N_{\mathrm{gas}} RT$



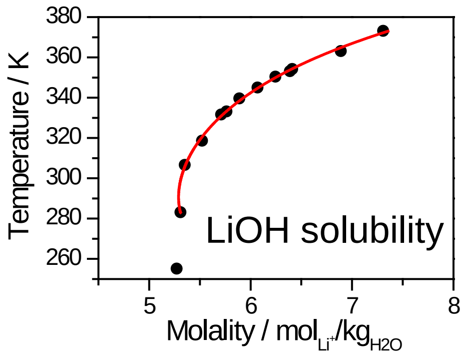
$J(s)$ Leverett Function
σ_t Surface tension
ε^0 Free volume fraction
k Permeability
μ Viscosity

Kumbur, E.C. *et al*. *J. Electrochem. Soc.* **154**, B1295 (2007).; Hao, L. *et al*. *Int. J. Heat Mass Transfer* **55**, 133–139, (2012).
Desnoyers, E. *et al*. *Can. J. Chem*. **62**, 878-885 (1984).; Herrington, T.M. *et al*. *J. Chem. Eng. Data* **31**, 31-34 (1986).; Millero, F.J. *et al*. *J. Acoust. Soc*. **61**, 1492-1498 (1977).

III. Model parameterization

- Thermodynamic parameters
  - $LiOH \cdot H_2O$ precipitation
  - ‚Salting-out' of oxygen

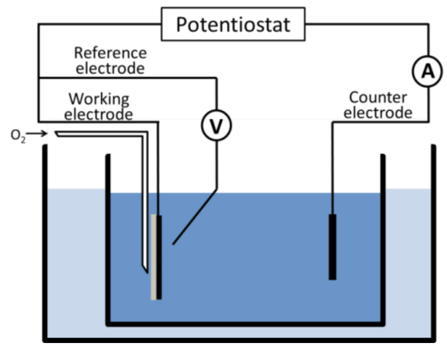
Literature

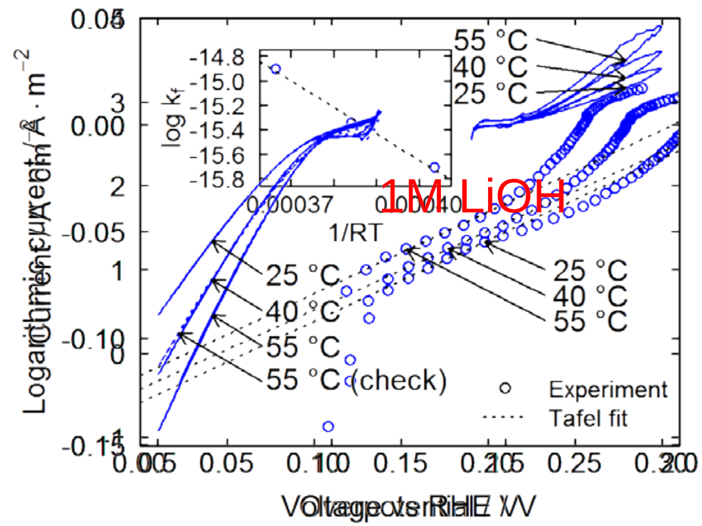


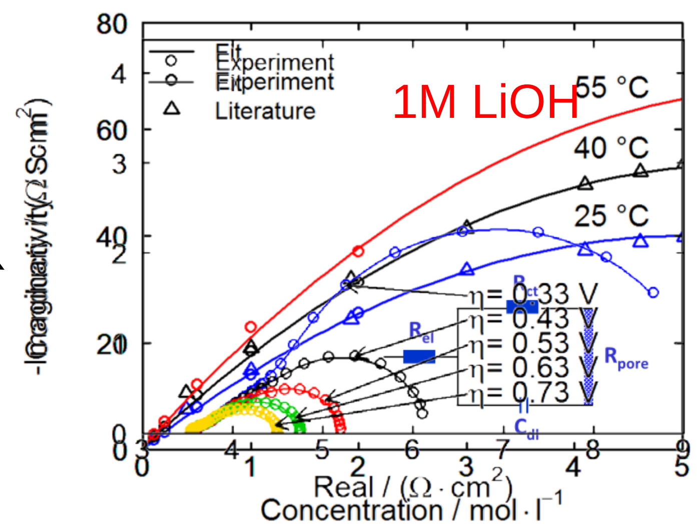
- Kinetic parameters
  - ORR/OER
- Structural parameters
  - Porosity, tortuosity, etc
- Transport parameters
  - Leverett function
  - Effective transport

III. Model parameterization – Electrochemical characterization

- **Three-electrode setup**
  - Alkaline LiOH solution (0.1-2M)
  - Pure oxygen (1 atm)
- **Ag-GDE** (commercial)
  - Defined structure
- Measurements
  - **CV, EIS**





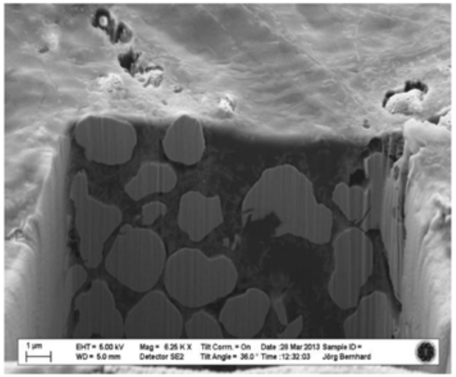


➔ Broad **parameter range** for parameterization and validation

Gierszewski *et al.*, Fusion Eng. Des., **13**, 59–71. (1990).
Light *et al.,* Electrochem. Solid-State Lett., **8**, E16. (2005).

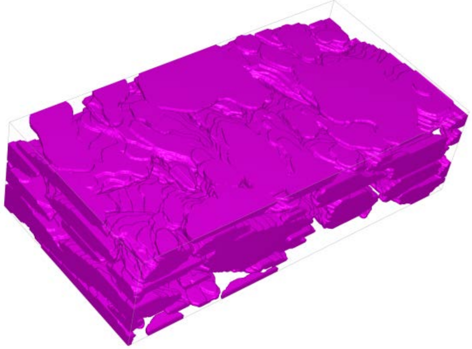
III. Model parameterization – Structural characterization

FIB-SEM



Binarization

Reconstruction



	Measurements	FIB-SEM
Porosity / -	0.479	0.495
d_{50} / µm	0.51	0.82
Specific surface area / m^{-1}	3.3×10^6	1.1×10^6

➔ Good agreement to experimental results

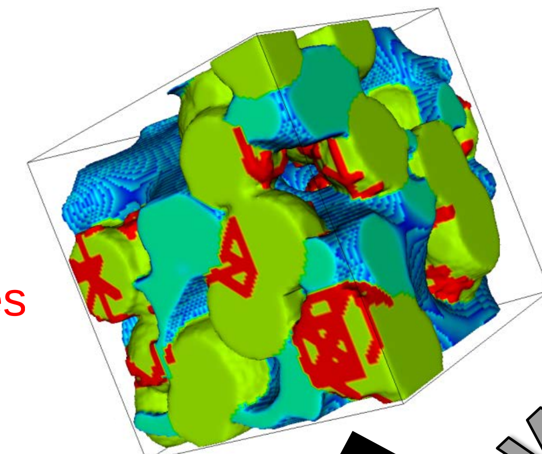
Collaboration with S.K. Eswara Moorthy,
Central Facility of Electron Microscopy, University of Ulm

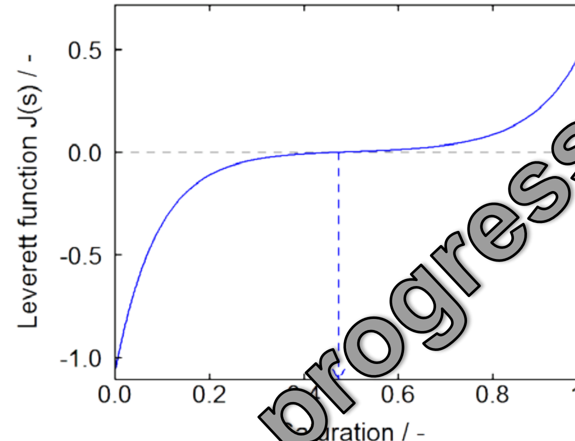
III. Model parameterization – Transport parameters

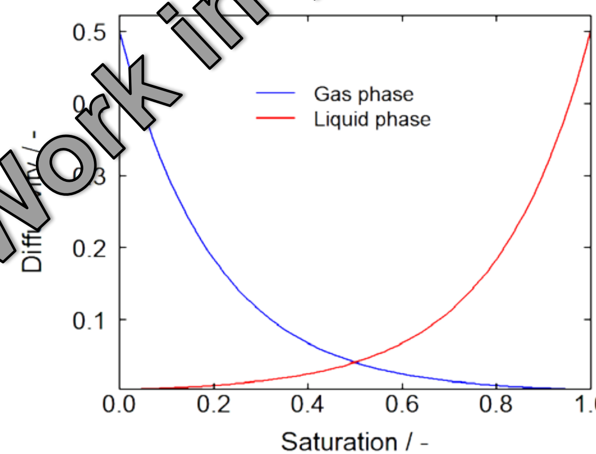
Collaboration with Prof. Arnulf Latz

Deutsches Zentrum für Luft- und Raumfahrt e.V.
German Aerospace Center

- **Lattice-Boltzmann modeling**
  - 2D and 3D simulations
  - SRT-BGK model
  - Multiphase simulations (Rothmann-Keller type)
  - Heterogeneous structures
- Simulation of p_c-S curves
- Effective transport properties







Work in progress

Initial code provided by **Prof. Volker Schulz** (DHBW Mannheim)

Liu, H. *et al. Physical Review E*, **85**, 046309 (2012).
Leclaire, *J Comput Phys*, **246**, 318–342 (2013).

III. Model parameterization

- Thermodynamic parameters
  - $LiOH \cdot H_2O$ precipitation
  - ‚Salting-out‘ of oxygen

  } Literature

- Kinetic parameters
  - ORR/OER

  } Half-cell experiments

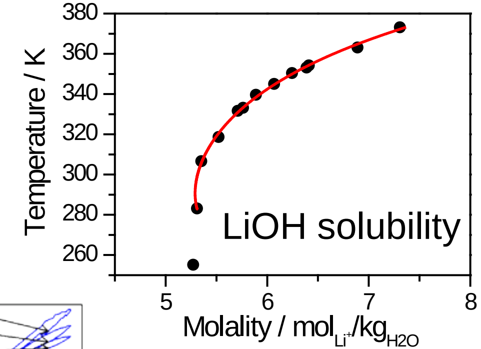
- Structural parameters
  - Porosity, tortuosity, etc

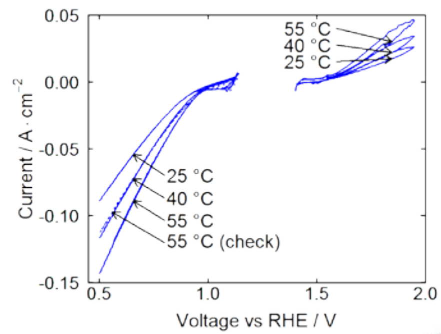
  } FIB-SEM

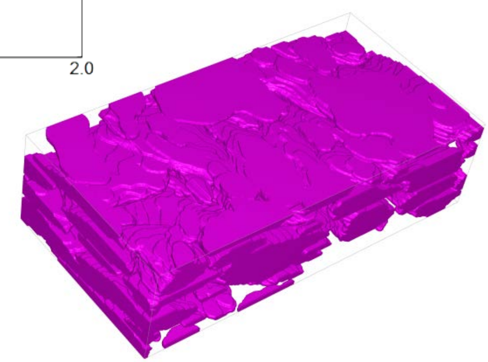
- Transport parameters
  - Leverett function
  - Effective transport

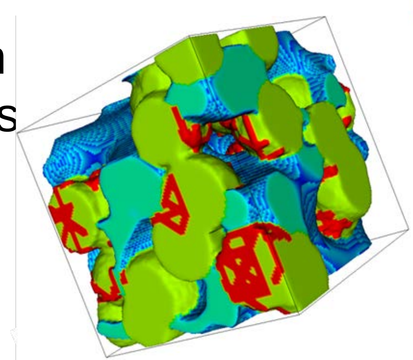
  } Lattice – Boltzmann simulations

➔ **Single set of parameters**





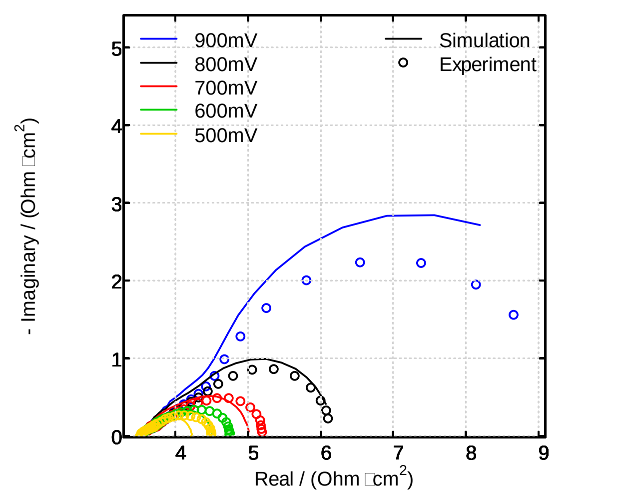




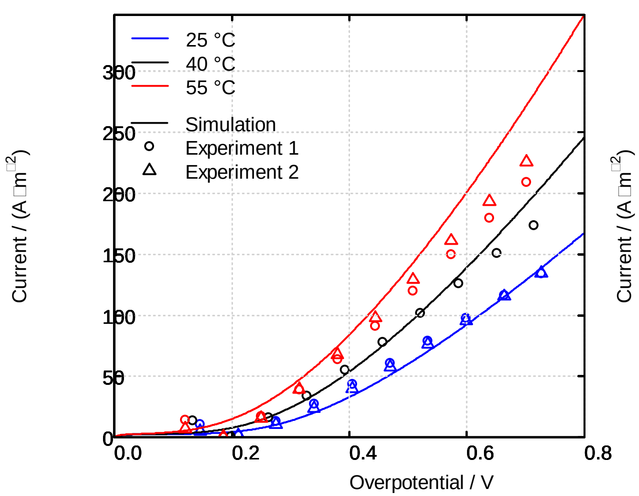
IV. Model validation

- IV curves and impedance spectra
  - ➔ **Good qualitative agreement**
- Deviation at high temperature, overpotential
  - Change in reaction mechanism?
  - Additional transport limitations?

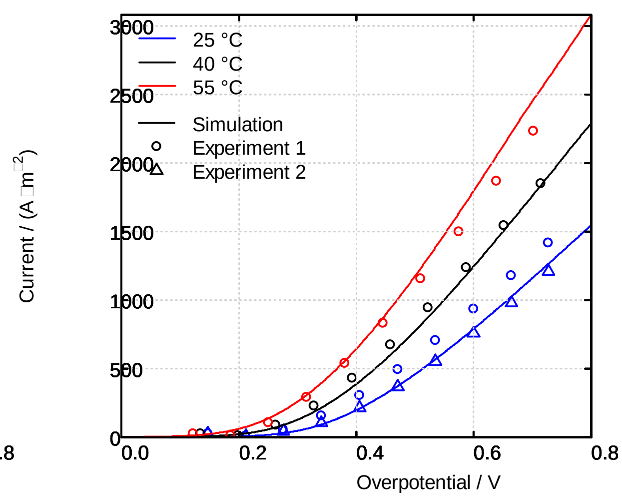
Nyquist plot - 1 M - 25 °C



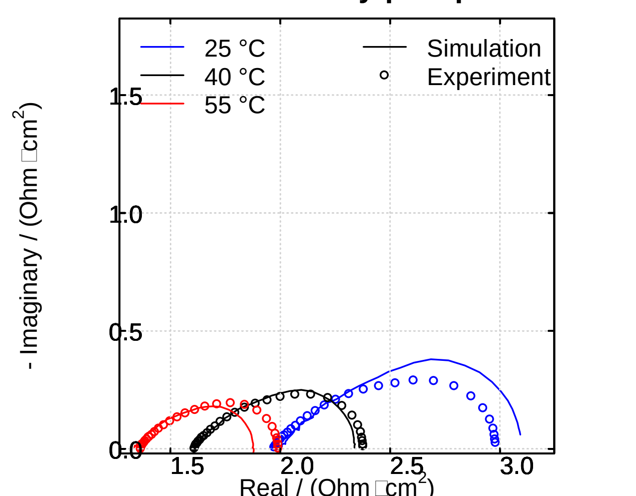
IV curves - 0.1 M LiOH



IV curves - 2 M LiOH



Nyquist plot - 2 M - 7



V. Electrode and cell design - Gas Diffusion Electrodes

- Sensitivity of current density

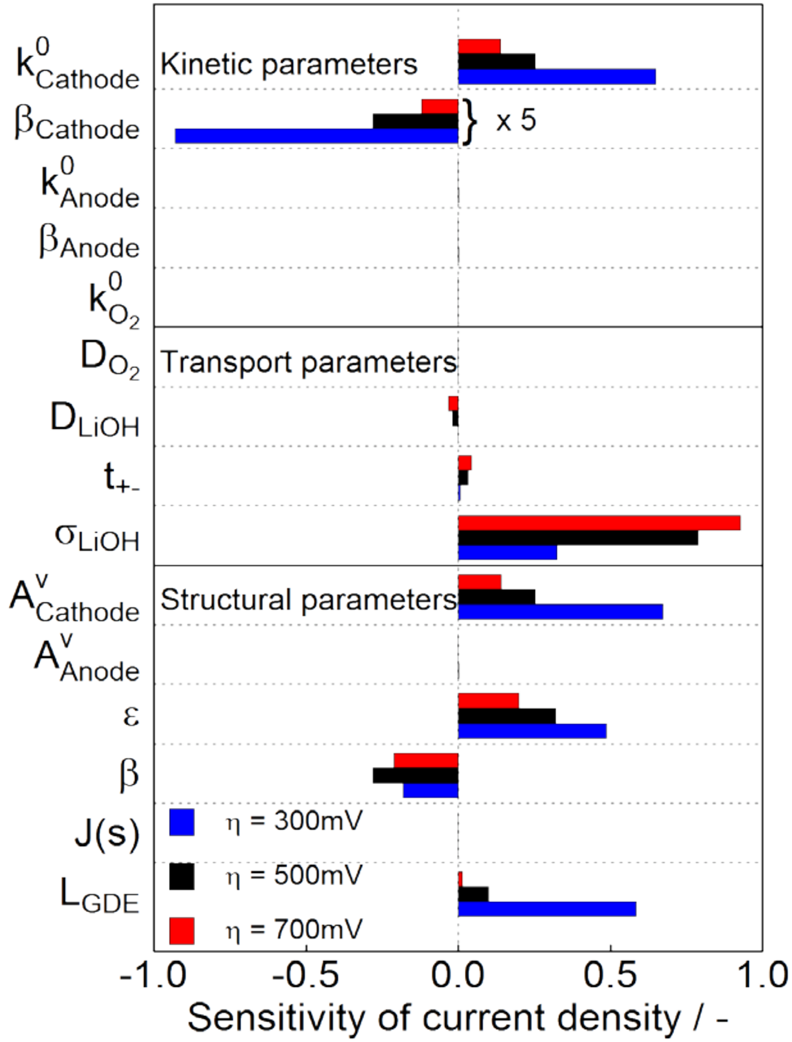
$$S_j = \frac{(i^0 - i^+)/i^0}{(\zeta^0 - \zeta^+)/\zeta^0}$$

- No influence of
  - Anode (three electrode setup)
  - O_2 pore-space transport (no liquid film modeled)
- High sensitivity of
  - Cathode kinetics (k^0, β)

  ➔ Development of new catalysts
  - Structural parameters (ε, τ, A^V)

  ➔ Optimization of GDE structure

➔ Validated 1D **model as design tool**



V. Electrode and cell design – Precipitation in aqueous Li-O_2 batteries

Horstmann, B., Danner, T., & Bessler, W. G.
Precipitation in aqueous lithium–oxygen batteries: a model-based analysis.
***Energy & Environmental Science*, *6*(4), 1299–1314. (2013).**

- **Classical theory of nucleation and growth**

$$Li^{+} + OH^{-} + H_2O \rightleftarrows LiOH{\cdot}H_2O^{(s)}$$

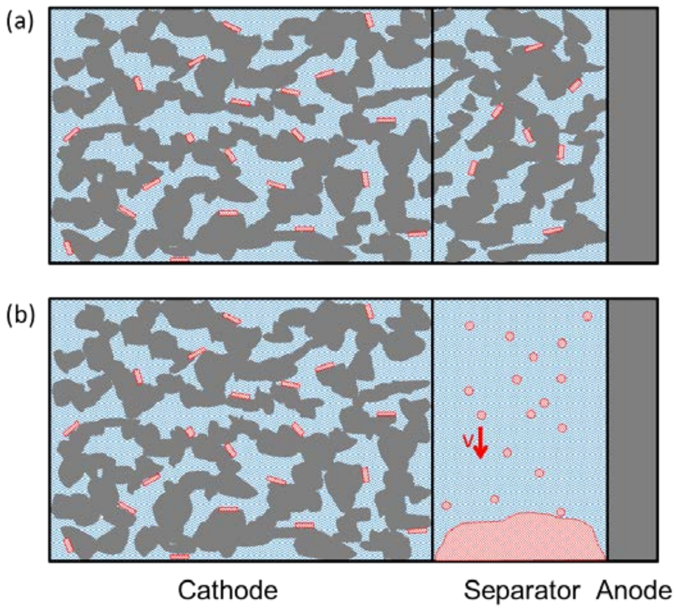
(a) Nucleation on **surfaces**

➔ Porous separator

(b) Nucleation on **dust** particles

➔ Bulk separator

➔ **Precipitation mainly on anode side**

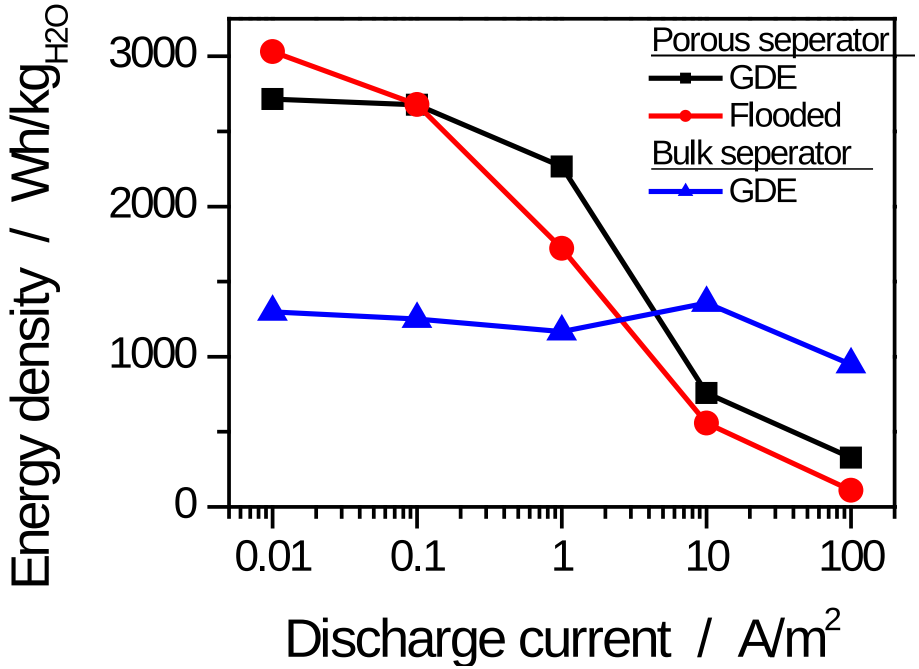


P. Stevens *et al.*, Development of a lithium air rechargeable battery, *ECS Transactions* **28**, 1 (2010).

III. Modeling and simulation – Precipitation in aqueous Li-O_2 batteries

- Evaluation of battery design
  - **Flooded** electrodes best at **low** rates
  - **Gas Diffusion Electrodes** best at **high** rates
  - **Bulk separator** superior at **very high** rates

➔ Precipitation as engineering task



➔ Design depends on operating conditions

IV. Summary

- **Model experiments on Ag GDEs**
  - Parameterization and validation
- FIB-SEM for **electrode reconstruction**
  - Structure determination
- **Lattice-Boltzmann** simulations
  - Multiphase flow
- Detailed model of **precipitation** in **aqueous** Li-O_2 batteries
  - ➔ Operating **conditions determine** battery **design**
- **Validation** of transport model
  - ➔ **Good qualitative agreement**

Thank you for your attention!